New Approaches to Reacting Flow Modeling for Endothermic Fuel Cracking and Combustion in High-Speed Combustion

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Objectives

Intermediate term

Mechanisms of early-stage homogeneous coking and methods to suppress PAH coalescence/ reaction.

Long term

Enable new approaches to kinetic modeling.

The Problem

Endothermic cooling system

- Fuel pyrolysis to remove heat
- Cracked products give better combustion performance
- Coke formation is a problem
- May use catalysts

JP7

Combustor

- Burns cracked fuel – composition coupled to cooling system operation and design
- Shocks and wide range of ϕ.
- Flame processes may be facilitated by the use of catalysts

- Fuel cracking in the cooling system gives heat sinking capability, but also promote coke formation.
    - Fuel cracking and coke formation driven by the same force – entropy!

Thermodynamic Driving Forces

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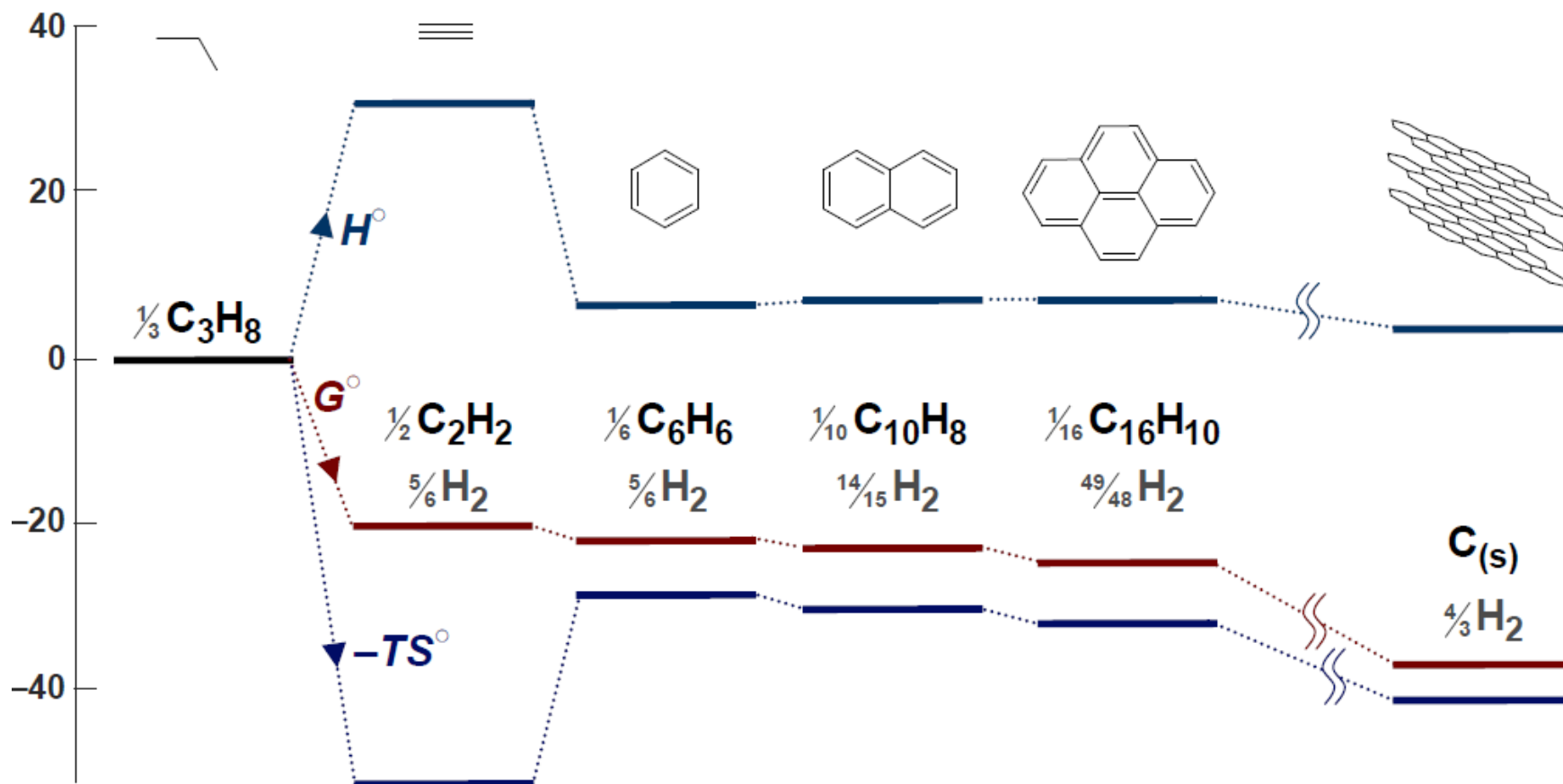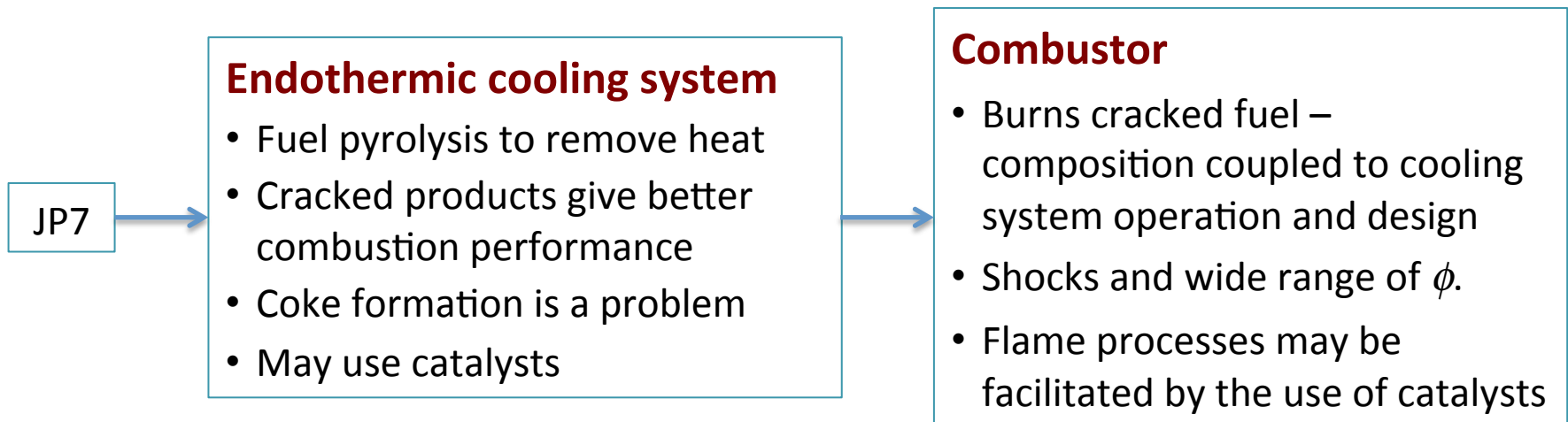
- Fuel cracking in cooling system gives heat sinking capability, but also promote coke formation.
  - Fuel cracking and coke formation driven by the same force – entropy!
  - The processes are kinetically controlled (and supercritical).
- Three types of coke deposits (**Edwards 2003**)
  - **Filamentous** – fluid/surface interactions in origin and controllable by surface materials engineering).
  - **Amorphous and graphitic** – PAHs formed in the fluid phase "coalesce" into particulates which deposit on walls – a key problem to be addressed.
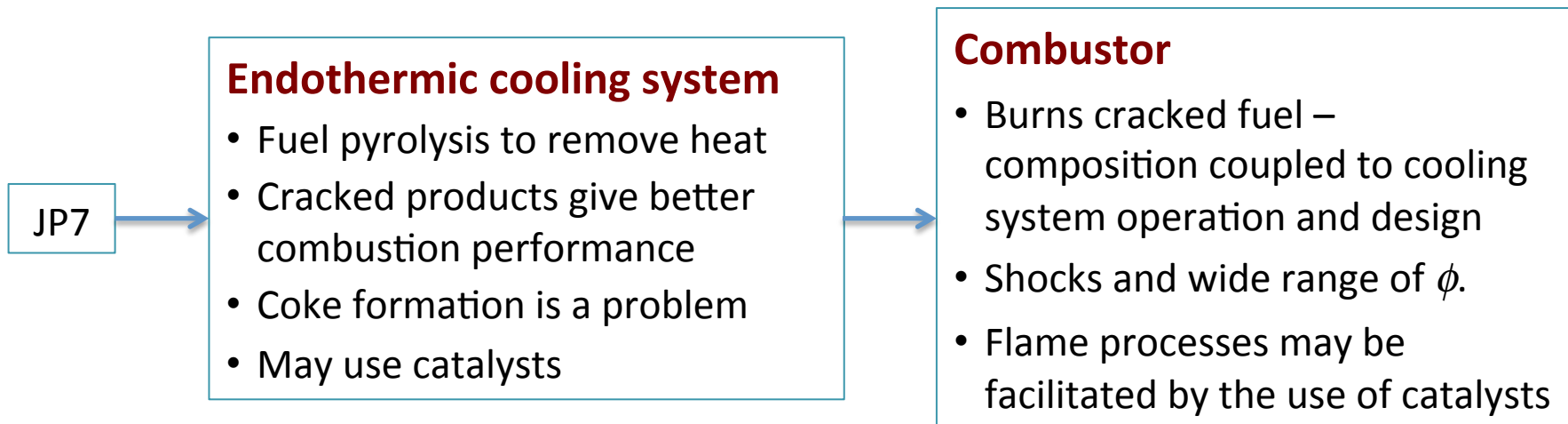
PAHs as Intermediates to Coke
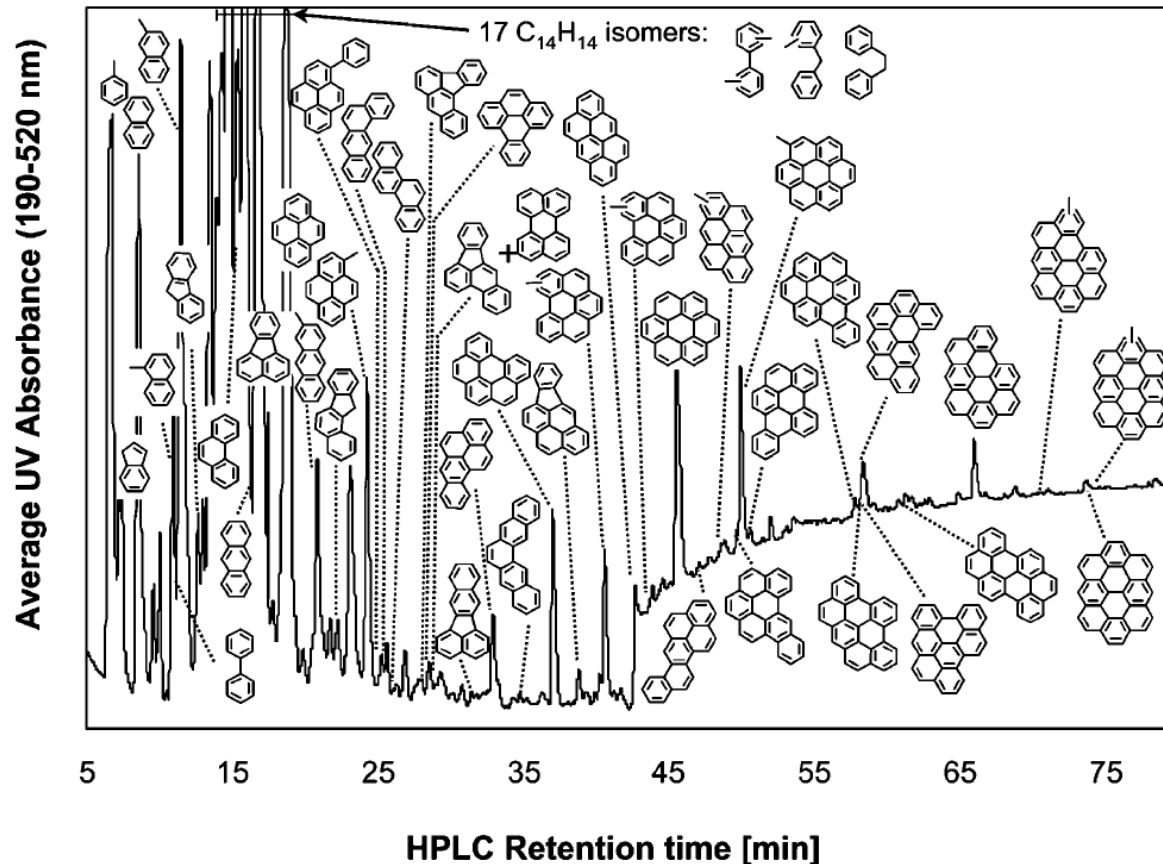
Wornat (2007)

- Amorphous and graphitic wall deposits are presumably from particulate matters due to PAH-PAH coalescence/reaction.

- PAH binding mechanisms not well established: dispersion/electrostatic interactions, excited states, dynamic bonding etc.

The Problem

JP7 →

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  - **Filamentous** – fluid/surface interactions in origin and controllable by surface materials engineering).
  - **Amorphous and graphitic** – PAHs formed in the fluid phase "coalesce" into particulates which deposit on walls – a key problem to be addressed.
- A highly coupled kinetic problem – how do we generate chemical reaction models directly from results of *ab initio* theory?

The Coking Problem

1. Fuel pyrolysis and PAH/coke formation share the same thermodynamic driving force. It is impossible to maximize fuel pyrolysis while suppress PAH formation at the same time.

2. Suppressing PAH-PAH coalescence/reaction is feasible, because such processes do not yield large Gibbs free energy drop.

    – Fundamental binding interactions among PAHs (purely dispersion/ electrostatic forces or also involves other *unknown* interactions – electronically excited states, π diradicals etc).

    – Dynamic effects under supercritical condition.

   – If these interactions/effects can be understood, is there an additive that can trick PAHs into disliking each other.

The Long-Term Combustion Chemistry Problem

1. Looking for an approach more robust and more "*ab initio*" than the current chemistry modeling approach.

   – Designs of endothermic cooling system and combustors are evolving;

   – New catalysts are being developed

   – Long lead-time to develop any predictive, coupled kinetic models

   – High pressure/supercritical kinetics – rate theory (and its application) falls apart.

   – ……

2. We have been using the approach of detailed kinetic modeling for more than 50 years.

   – Is this the only "fundamental" approach we can take?

   – Do we need to write out thousands of reactions before we can make a prediction about the kinetic and heat release rates?

Potential Energy Landscape and Associated Approaches

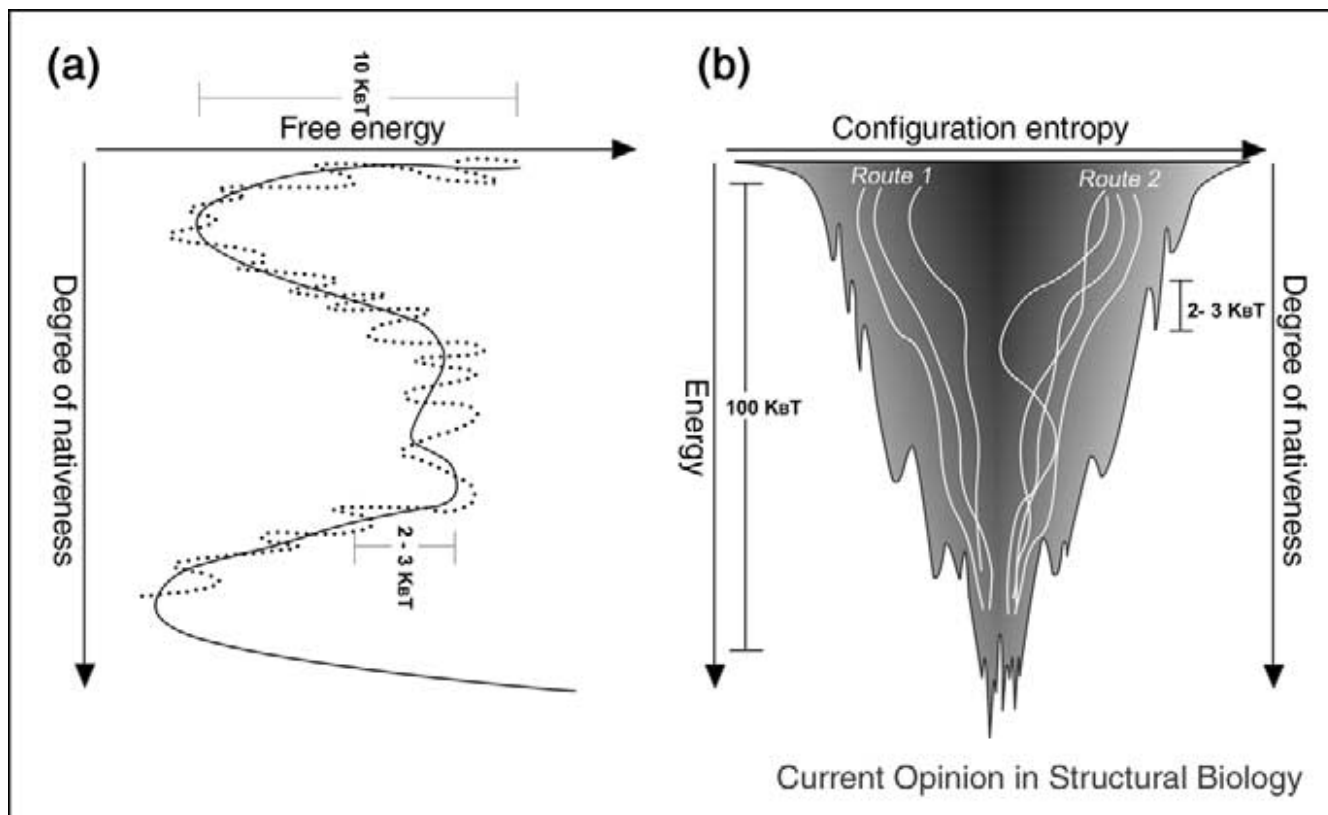- A concept widely used in protein folding kinetics (Joseph Bryngelson)
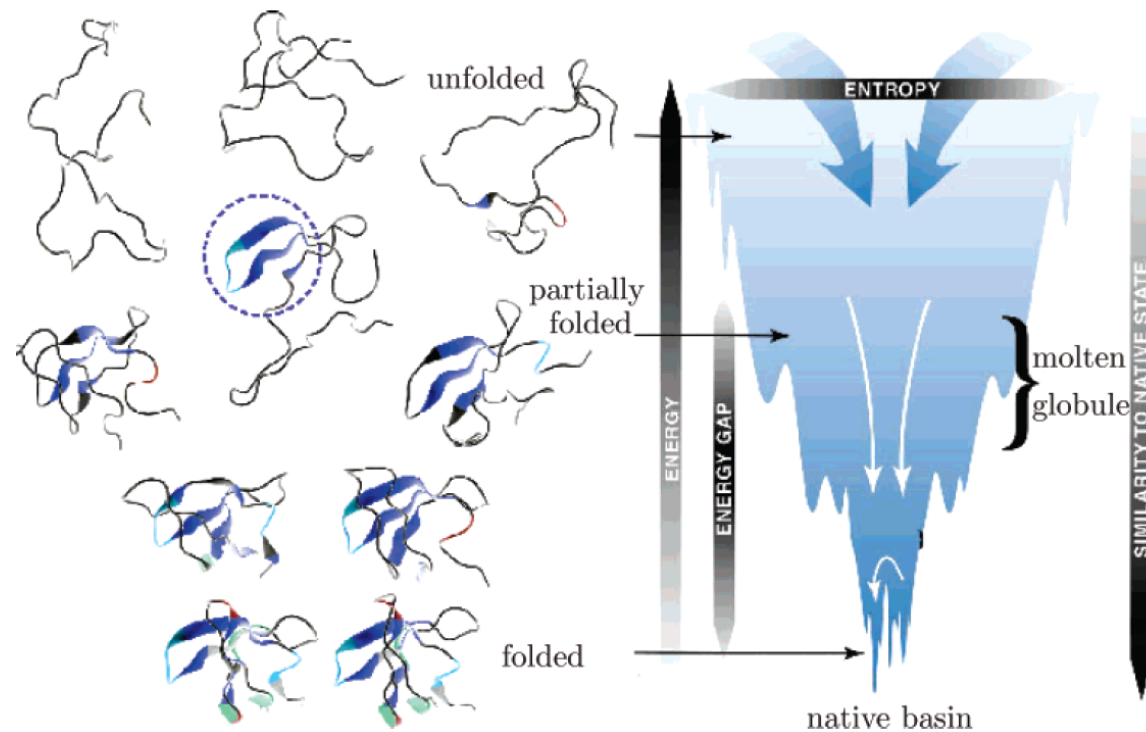
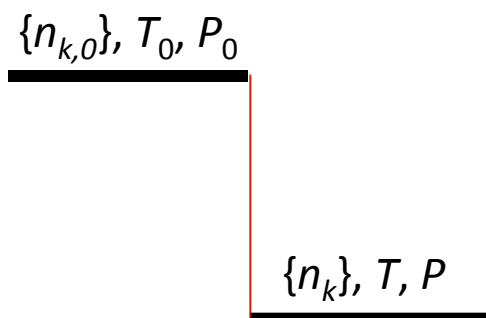Wales & Bogdan *JPCB* (2006)

- and in materials/fuel cell research.

Potential Energy Landscape and Associated Approaches

- **Accuracy of kinetic prediction may be improved, as needed, by adapting the resolution of potential energy.**

Onuchic & Wolynes *Current Opinion in Structural Biology* (2004)

RCCE and Potential Energy Landscaping (RCCE-PEL)

$\{n_{k,0}\}, T_0, P_0$

$\{n_k\}, T, P$

0th order potential energy landscape

- No reaction steps → Infinite rate kinetics

- The end state represents chemical equilibrium

$\{n_{k,0}\}, T_0, P_0$

$\{n_{k,0}\}, T_0, P_0$

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$\{n_k\}, T, P$
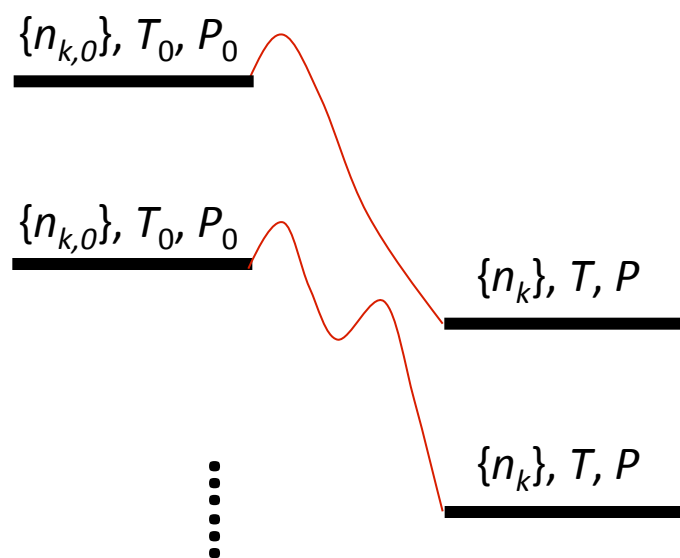
Higher-order potential energy landscapes

- Slow(er) reaction steps added – equivalent to adding details (barriers and local minima) into the potential energy landscape

- Finite rate kinetics with accuracy improved by an adaptive approach to adding PES details

- Converging chemical time scale ⟷ physical time scale (flow, turbulence, transport)

The Team

Guillaume Blanquart
CalTech

- PEL-RCCE in turbulent reacting flow modeling

Ronald K. Hanson
Stanford

- Experimental method developments
  $T(t)$, $H(t)$, $S(t)$, $G(t)$

William L. Hase
Texas Tech

- Chemical dynamics
  aromatic interactions and binding
  post-transition state dynamics

Keiji Morokuma
Emory/Kyoto U.

- Automated PES search methods

Hai Wang
USC

- PEL-RCCE theory and application
- PAH-PAH binding interactions/coalescence
  suppression
- Nanocatalysts

Rate-Controlled Constrained-Equilibrium (RCCE)

Keck & Gillespie (1971); Keck (1990); Beretta et al. (2012)

The method of Lagrange Multipliers as applied to chemical equilibrium

$$L = \frac{G}{R_u T} + \sum_{m=1}^{M} \lambda_m \left(\sum_{k=1}^{K} a_{mk} n_k - e_m \right)$$

The equilibrium composition is given as

$$n_k = n_0 \exp \left[-\frac{g_k^o(T)}{R_u T} - \ln \frac{p}{p^0} - \sum_{m=1}^{M} \lambda_m a_{mk} \right]$$

$$= n_0 Q_k \exp \left[-\sum_{m=1}^{M} \lambda_m a_{mk} \right]$$

where the multipliers are solved by

$$e_m = n_0 \sum_{k=1}^{K} a_{mk} Q_k \exp \left[-\sum_{m=1}^{M} \lambda_m a_{mk} \right] \quad (m = 1, \ldots M \text{ elements})$$

$$1 = \sum_{k=1}^{K} Q_k \exp \left[-\sum_{m=1}^{M} \lambda_m a_{mk} \right]$$

Rate-Controlled Constrained-Equilibrium (RCCE)

Keck & Gillespie (1971); Keck (1990); Beretta et al. (2012)

For non-equilibrium problems, additional constraints are added as needed, preferably starting from rate limiting steps:

$$e_l = \sum_{k=1}^{K} a_{lk} n_k \quad (l - m = 1, ... R)$$

$$\frac{d(e_l/V)}{dt} = \sum_{k=1}^{K} a_{lk} \frac{d(n_k/V)}{dt}$$

$$= \sum_{k=1}^{K} a_{lk} \left(\sum_{l=1}^{s_l} \nu_{kl} R_{lf} - \sum_{l=1}^{s_l} \nu'_{kl} R_{lb} \right)$$

- Yields the exact solution when the number of constraining equations R = number of reactions I (Keck 1990).

- Good quality, converging solution achieved usually with $R \ll I$.

- A mechanism reduction method – allowing for separation of time scales – still require a (detailed) reaction mechanism to be made available.

Principle Questions Yet to be Addressed

- Can a potential energy landscape (PEL) approach be developed from ab initio methods?

- Can the rate limiting steps on the PEL be identified in a robust manner?

- Can new experimental approaches be developed to interrogate parts of a PEL?

- What are the role of the better known H_2/C_1-C_4 chemistry in the RCCE-PEL approach?

- Can the RCCE-PEL approach be implemented in turbulent flame simulations?

Current Approach

- **Methodology based on Dixon-Lewis's work in the 1960s'.**
  - Write down every reaction step and find its rate coefficient.
  - H_2, H_2/CO etc with ~ 2 dozen reactions.
  - Can have a closure because of a limited number of rate parameters.
  - Allowed us to understand the detailed laminar flame structure.

- **Later work by many focused on combustion chemistry of small hydrocarbons – O(100) reactions – many of which have been probed directly by experiments and rate theory calculations.**

- **Recent effort for large hydrocarbons largely based on empirical knowledge**
  - group additivity
  - analogous reactions – reaction class
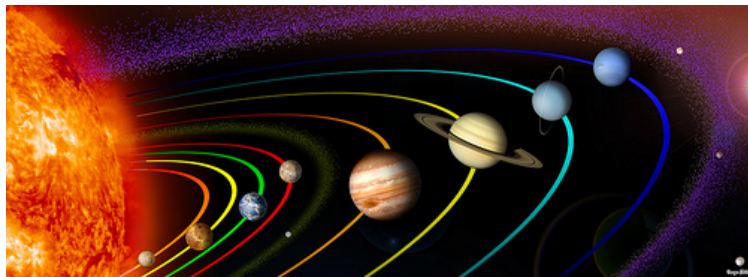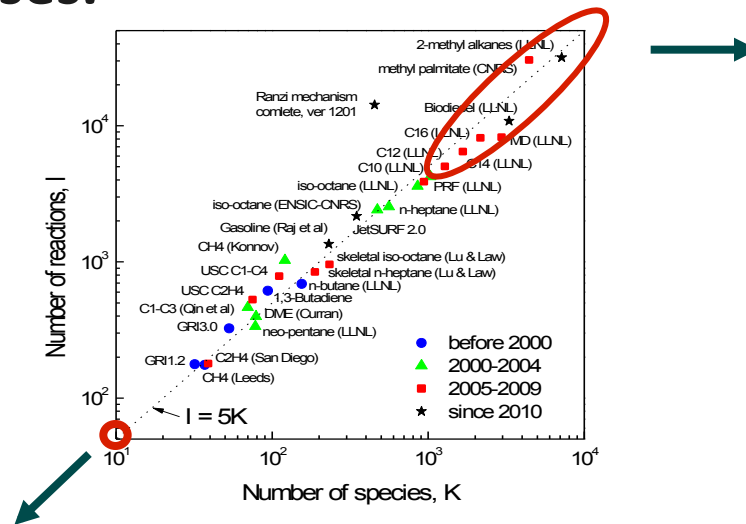 - guesses

Current Approach

• **The number of species/reactions increases exponentially as the fuel size increases.**
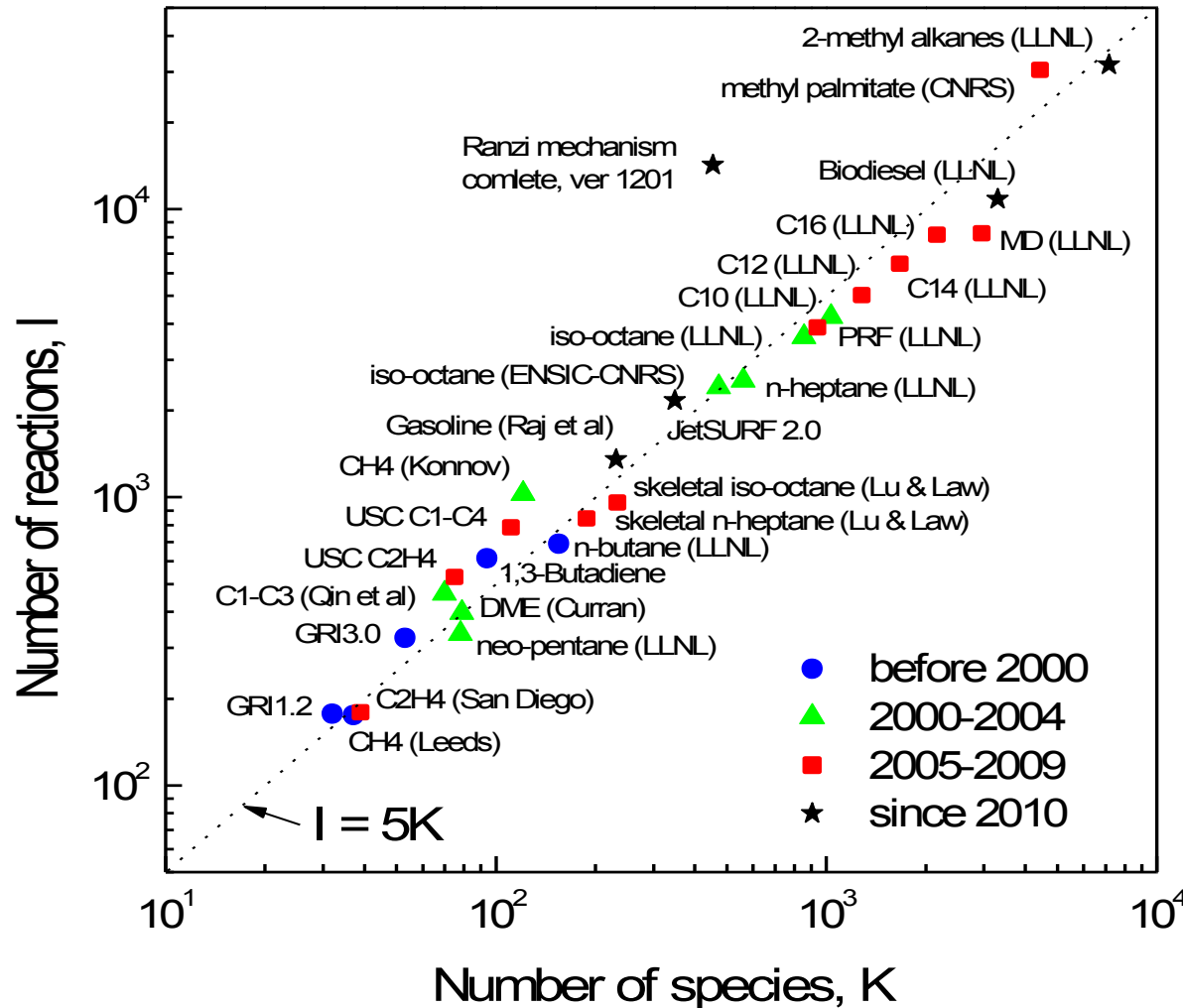
An updated version of Lu & Law, 2009

Current Approach

- **The number of species/reactions increases exponentially as the fuel size increases.**

- A solar system model built on the position and velocity of each and every planet is a triumph of science.

- A milky-way galaxy model built on the position and velocity of each plant and star is probably a terrible model.

Combustion Reaction Mechanism Development

- **Methods of mechanism reduction becomes mature.**
  - Still require detailed reaction models to be made available
  - The number of scalars remain large, perhaps too large to incorporate in CFD codes (high-speed combustion) for years to come

- **Rethink our strategy for treating chemistry.**
  - Adaptive resolution/accuracy
  - Key property to follow: time evolution of energy and entropy

  - Throw away the concept of reaction mechanism for the moment
  - Focus on the potential energy surface
    some initial thoughts in the context of Keck's RCCE